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Midwest Research Inst., Kansas City, MO

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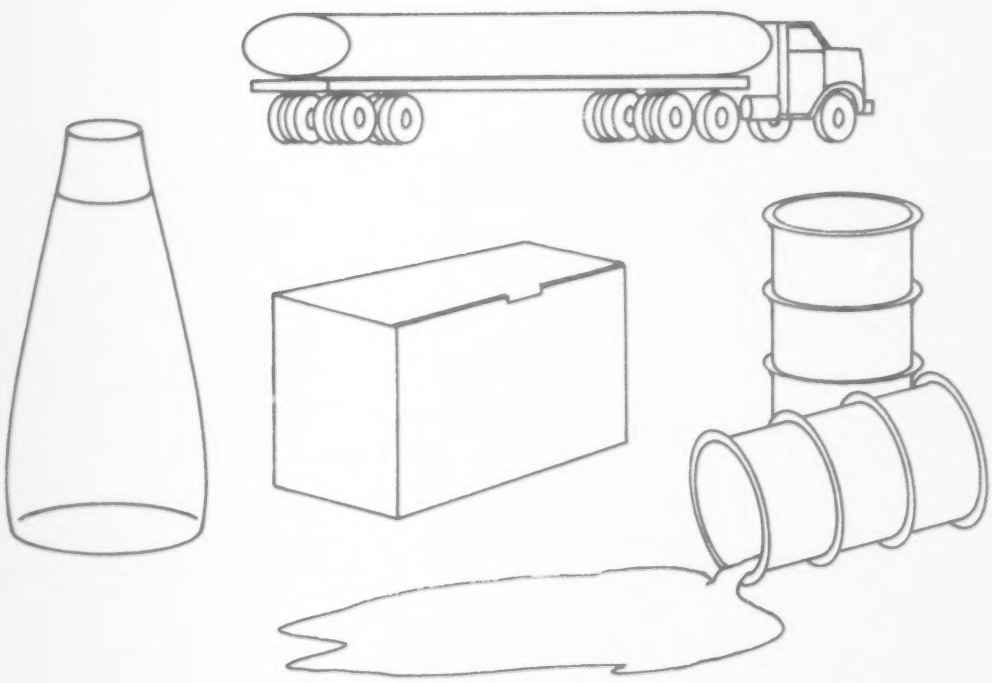

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16. ABSTRACT

This is a gas chromatographic/electron impact mass spectrometric (GC/EIMS) method applicable to the determination of chlorinated biphenyls (PCBs) in commercial products and product wastes. The PCBs present may originate either as synthetic by-products or as contaminants derived from commercial PCB products (e.g., Aroclors). The PCBs may be present as single isomers or complex mixtures and may include all 209 congeners from monochlorobiphenyl through decachlorobiphenyl.

A variety of general and specific sample preparation options are presented in this method. This method takes a different approach from those which rely on Aroclor mixtures for calibration and quantitation. In this method PCBs are detected and quantitated by homolog group. The results can be summed to give a total PCB value comparable to results generated by other methods or they may be presented as 10 individual homolog values. This homolog distribution can provide additional quantitative information on the composition and source of the PCBs.

The method performance is assessed for each sample. A set of four ^{13}C-labeled PCBs is employed as recovery surrogates. If the surrogates are recovered and other QC parameters are within acceptable limits, then the data may be considered valid.

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ANALYTICAL METHOD: THE ANALYSIS OF BY-PRODUCT CHLORINATED BIPHENYLS IN COMMERCIAL PRODUCTS AND PRODUCT WASTES, REVISION 2

by

Mitchell D. Erickson

WORK ASSIGNMENT NO. 6

SPECIAL REPORT NO. 1

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For

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Office of Toxic Substances
Field Studies Branch, TS-798
401 M Street, SW
Washington, DC 20460

Attn: Joseph J. Breen, Project Officer
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This document has been reviewed and approved for publication by the Office of Toxic Substances, Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency. The use of trade names or commercial products does not constitute Agency endorsement or recommendation for use.

PREFACE

This report contains an analytical method for the analysis of by-product polychlorinated biphenyls in commercial products and wastes. The work was done on Work Assignment No. 6 on U.S. Environmental Protection Agency Contract No. 68-02-3938. This is the second revision of the method. Previous revisions are cited as references 3 and 4 in the method. This report was prepared by Mitchell Erickson. The work on the previous revisions was conducted by Dr. Erickson, John Stanley, Kay Turman, Gil Radolovich, Karin Bauer, Jon Onstot, Donna Rose, Margaret Wickham, and Ruth Blair. The work for the previous revisions was performed on Task 51 of EPA Contract No. 68-01-5915.

Two companion methods have been published which address air (Special Report No. 2, EPA Report No. EPA-560/5-85-011) and water (Special Report No. 3, EPA Report No. EPA-560-5-85-012).

The EPA Work Assignment Manager, Daniel T. Heggem, of Field Studies Branch provided helpful guidance.

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THE ANALYSIS OF BY-PRODUCT CHLORINATED BIPHENYLS IN COMMERCIAL PRODUCTS AND PRODUCT WASTES

1.0 Scope and Application

1.1 This is a gas chromatographic/electron impact mass spectrometric (GC/EIMS) method applicable to the determination of chlorinated biphenyls (PCBs) in commercial products and product wastes. The PCBs present may originate either as synthetic by-products or as contaminants derived from commercial PCB products (e.g., Aroclors). The PCBs may be present as single isomers or complex mixtures and may include all 209 congeners from monochlorobiphenyl through decachlorobiphenyl listed in Table 1.

This method was prepared for use in demonstrating compliance with the EPA rules regarding the generation of PCBs as by-products in commercial chemical production[1,2] and is based on earlier versions.[3,4] This revision includes elimination of a calculation which corrects the native PCB concentration based on the recovery of the ^{13}C-labeled PCB recovery surrogates. In addition, full scan is now emphasized over the selected ion monitoring and limited mass scan mass spectrometric data collection modes. The latter two techniques provide less qualitative information and should be used only if needed to achieve the required sensitivity. Additional background information on selection of the techniques has also been published.[5]

1.2 The detection and quantitation limits are dependent upon the complexity of the sample matrix and the ability of the analyst to remove interferents and properly maintain the analytical system. For low level PCBs (0.05 to 0.2 µg/g), the method precision appears to be about ± 60% based on a very limited study. The method performance at higher levels (e.g., 2 µg/g) will be determined in future studies.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography/mass spectrometry (GC/MS) and in the interpretation of gas chromatograms and mass spectra. Prior to sample analysis, each analyst must demonstrate the ability to generate acceptable results with this method by following the procedures described in Section 15.2.

1.4 The validity of the results depends on equivalent recovery of the analyte and ^{13}C PCBs. If the ^{13}C PCBs are not thoroughly incorporated in the matrix, the method is not applicable.

TABLE 1. NUMBERING OF PCB CONGENERS[a]

No.	Structure
	Monochlorobiphenyls
1	2
2	3
3	4
	Dichlorobiphenyls
4	2,2'
5	2,3
6	2,3'
7	2,4
8	2,4'
9	2,5
10	2,6
11	3,3'
12	3,4
13	3,4'
14	3,5
15	4,4'
	Trichlorobiphenyls
16	2,2',3
17	2,2',4
18	2,2',5
19	2,2',6
20	2,3,3'
21	2,3,4
22	2,3,4'
23	2,3,5
24	2,3,6
25	2,3',4
26	2,3',5
27	2,3',6
28	2,4,4'
29	2,4,5
30	2,4,6
31	2,4',5
32	2,4',6
33	2',3,4
34	2',3,5
35	3,3',4
36	3,3',5
37	3,4,4'
38	3,4,5
39	3,4',5
	Tetrachlorobiphenyls
40	2,2',3,3'
41	2,2',3,4
42	2,2',3,4'
43	2,2',3,5
44	2,2',3,5'
45	2,2',3,6
46	2,2',3,6'
47	2,2',4,4'
48	2,2',4,5
49	2,2',4,5'
50	2,2',4,6
51	2,2',4,6'
	Tetrachlorobiphenyls
52	2,2',5,5'
53	2,2',5,6'
54	2,2',6,6'
55	2,3,3',4
56	2,3,3',4'
57	2,3,3',5
58	2,3,3',5'
59	2,3,3',6
60	2,3,4,4'
61	2,3,4,5
62	2,3,4,6
63	2,3,4',5
64	2,3,4',6
65	2,3,5,6
66	2,3',4,4'
67	2,3',4,5
68	2,3',4,5'
69	2,3',4,6
70	2,3',4',5
71	2,3',4',6
72	2,3',5,5'
73	2,3',5',6
74	2,4,4',5
75	2,4,4',6
76	2',3,4,5
77	3,3',4,4'
78	3,3',4,5
79	3,3',4,5'
80	3,3',5,5'
81	3,4,4',5
	Pentachlorobiphenyls
82	2,2',3,3',4
83	2,2',3,3',5
84	2,2',3,3',6
85	2,2',3,4,4'
86	2,2',3,4,5
87	2,2',3,4,5'
88	2,2',3,4,6
89	2,2',3,4,6'
90	2,2',3,4',5
91	2,2',3,4',6
92	2,2',3,5,5'
93	2,2',3,5,6
94	2,2',3,5',6
95	2,2',3,5',6
96	2,2',3,6,6'
97	2,2',3',4,5
98	2,2',3',4,6
99	2,2',4,4',5
100	2,2',4,4',6
101	2,2',4,5,5'
102	2,2',4,5,6'
103	2,2',4,5',6
104	2,2',4,6,6'
	Pentachlorobiphenyls
105	2,3,3',4,4'
106	2,3,3',4,5
107	2,3,3',4',5
108	2,3,3',4,5'
109	2,3,3',4,6
110	2,3,3',4',6
111	2,3,3',5,5'
112	2,3,3',5,6
113	2,3,3',5',6
114	2,3,4,4',5
115	2,3,4,4',6
116	2,3,4,5,6
117	2,3,4',5,6
118	2,3',4,4',5
119	2,3',4,4',6
120	2,3',4,5,5'
121	2,3',4,5',6
122	2',3,3',4,5
123	2',3,4,4',5
124	2',3,4,5,5'
125	2',3,4,5,6'
126	3,3',4,4',5
127	3,3',4,5,5'
	Hexachlorobiphenyls
128	2,2',3,3',4,4'
129	2,2',3,3',4,5
130	2,2',3,3',4,5'
131	2,2',3,3',4,6
132	2,2',3,3',4,6'
133	2,2',3,3',5,5'
134	2,2',3,3',5,6
135	2,2',3,3',5,6'
136	2,2',3,3',6,6'
137	2,2',3,4,4',5
138	2,2',3,4,4',5'
139	2,2',3,4,4',6
140	2,2',3,4,4',6'
141	2,2',3,4,5,5'
142	2,2',3,4,5,6
143	2,2',3,4,5,6'
144	2,2',3,4,5',6
145	2,2',3,4,6,6'
146	2,2',3,4',5,5'
147	2,2',3,4',5,6
148	2,2',3,4',5,6'
149	2,2',3,4',5',6
150	2,2',3,4',6,6'
151	2,2',3,5,5',6
152	2,2',3,5,6,6'
153	2,2',4,4',5,5'
154	2,2',4,4',5,6'
155	2,2',4,4',6,6'
156	2,3,3',4,4',5
157	2,3,3',4,4',5'
158	2,3,3',4,4',6
159	2,3,3',4,5,5'
160	2,3,3',4,5,6
	Hexachlorobiphenyls
161	2,3,3',4,5',6
162	2,3,3',4',5,5'
163	2,3,3',4',5,6
164	2,3,3',4',5',6
165	2,3,3',5,5',6
166	2,3,4,4',5,6
167	2,3',4,4',5,5'
168	2,3',4,4',5',6
169	3,3',4,4',5,5'
	Heptachlorobiphenyls
170	2,2',3,3',4,4',5
171	2,2',3,3',4,4',6
172	2,2',3,3',4,5,5'
173	2,2',3,3',4,5,6
174	2,2',3,3',4,5,6'
175	2,2',3,3',4,5',6
176	2,2',3,3',4,6,6'
177	2,2',3,3',4',5,6
178	2,2',3,3',5,5',6
179	2,2',3,3',5,6,6'
180	2,2',3,4,4',5,5'
181	2,2',3,4,4',5,6
182	2,2',3,4,4',5,6'
183	2,2',3,4,4',5',6
184	2,2',3,4,4',6,6'
185	2,2',3,4,5,5',6
186	2,2',3,4,5,6,6'
187	2,2',3,4',5,5',6
188	2,2',3,4',5,6,6'
189	2,3,3',4,4',5,5'
190	2,3,3',4,4',5,6
191	2,3,3',4,4',5',6
192	2,3,3',4,5,5',6
193	2,3,3',4',5,5',6
	Octachlorobiphenyls
194	2,2',3,3',4,4',5,5'
195	2,2',3,3',4,4',5,6
196	2,2',3,3',4,4',5,5'
197	2,2',3,3',4,4',5,6'
198	2,2',3,3',4,5,5',6
199	2,2',3,3',4,5,6,6'
200	2,2',3,3',4,5',6,6'
201	2,2',3,3',4,5,5',5'
202	2,2',3,3',5,5',6,6'
203	2,2',3,4,4',5,5',6
204	2,2',3,4,4',5,6,6'
205	2,3,3',4,4',5,5',6
	Nonachlorobiphenyls
206	2,2',3,3',4,4',5,5',6
207	2,2',3,3',4,4',5,6,6'
208	2,2',3,3',4,5,5',6,6'
	Decachlorobiphenyl
209	2,2',3,3'4,4',5,5',6,6'

[a]Adopted from Ballschmiter, K. and Zell, M., Fresenius Z. Anal. Chem., 302, 20-31 (1980).

1.5 During the development and testing of this method, certain analytical parameters and equipment designs were found to affect the validity of the analytical results. Proper use of the method requires that such parameters or designs must be used as specified. These items are identified in the text by the word "must." Anyone wishing to deviate from the method in areas so identified must demonstrate that the deviation does not affect the validity of the data. Alternative test procedure approval must be obtained from the Agency. An experienced analyst may make modifications to parameters or equipment identified by the term "recommended." Each time such modifications are made to the method, the analyst must repeat the procedure in Section 15.2. In this case, formal approval is not required, but the documented data from Section 15.2 must be on file as part of the overall quality assurance program.

1.6 This method contains many options because of the diversity of matrices and interferences which may be encountered. Once the appropriate options for each sample type have been selected, each laboratory should prepare a written step-by-step protocol for use by the analysts. The protocol may contain verbatim sections from this method, more detailed steps for certain techniques, or totally different extraction or cleanup techniques.

2.0 Summary

2.1 The process or product must be sampled such that the specimen collected for analysis is representative of the whole. Statistically designed selection of the sampling position, time, or discrete product units should be employed. The sample must be preserved to prevent PCB loss prior to analysis. Customary inventory storage may be adequate for products. For intermediates, process samples, and other non-product specimens, other preservation techniques may be needed.

2.2 The sample is mechanically homogenized and subsampled if necessary. The sample must then be spiked with four ^{13}C PCB surrogates (4-chloro-$^{13}C_6$-biphenyl; 3,3',4,4'-tetrachloro-$^{13}C_{12}$-biphenyl; 2,2',3,3',-5,5',6,6'-octachloro-$^{13}C_{12}$-biphenyl; and decachloro-$^{13}C_{12}$-biphenyl) and the surrogates incorporated by further mechanical agitation.

2.3 The surrogate-spiked sample is extracted and cleaned up at the discretion of the analyst. Simple dilution or direct injection is permissible. Possible extraction techniques include liquid-liquid partition, thermal desorption, and sorption onto resin columns followed by solvent desorption. Cleanup techniques may include liquid-liquid partition, sulfuric acid cleanup, saponification, adsorption chromatography, high performance liquid chromatography, gel permeation chromatography, or a combination of cleanup techniques. The sample is diluted or concentrated to a final known volume for instrumental determination.

2.4 The PCB content of the sample extract must be determined by high resolution (preferred) or packed column gas chromatography/electron impact mass spectrometry (HRGC/EIMS or PGC/EIMS) operated in the full scan, selected ion monitoring (SIM), or limited mass scan (LMS) mode.

2.5 PCBs are identified by comparison of their retention time and mass spectral intensity ratios to those in calibration standards.

2.6 PCBs are quantitated by the internal standard technique, using response factors for a mixture of 10 PCB congeners. The recoveries of four ^{13}C surrogates are used to monitor for losses in workup and determination.

2.7 The PCBs identified by the SIM technique may be confirmed by full scan HRGC/EIMS, retention on alternate GC columns, other mass spectrometric techniques, infrared spectrometry, or other techniques, provided that the sensitivity and selectivity of the technique are demonstrated to be comparable or superior to GC/EIMS.

2.8 The analysis time is dependent on the extent of workup employed. The time required for instrumental analysis of a single sample, excluding instrumental calibration, data reduction and reporting, is typically 30 to 45 min.

2.9 A quality assurance (QA) plan must be developed for each laboratory.

2.10 Quality control (QC) measures include laboratory certification and performance check sample analysis, procedural QC (instrumental performance, calculation checks), and sample QC (blanks, replicates, and standard addition).

3.0 Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware, leading to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences by the analysis of laboratory reagent blanks as described in Section 15.0.

3.1.1 Glassware must be scrupulously cleaned. All glassware should be cleaned as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water and rinses with tap water and reagent water. The glassware should then be drained dry and heated in a muffle furnace at 400°C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be

substituted for the muffle furnace heating. Volumetric ware should not be heated in a muffle furnace. After it is dry and cool, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. It is stored inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required. All solvent lots must be checked for purity prior to use.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the sources of samples.

4.0 Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis.

4.2 Polychlorinated biphenyls have been tentatively classified as known or suspected human or mammalian carcinogens. Primary standards of these toxic compounds should be prepared in a hood. Personnel must wear protective equipment, including gloves and safety glasses.

Congeners highly substituted at the meta and para positions and unsubstituted at the ortho positions are reported to be the most toxic. Extreme caution should be taken when handling these compounds neat or in concentrated solutions. This class includes 3,3',4,4'-tetrachlorobiphenyl (both natural abundance and isotopically labeled).

4.3 Diethyl ether should be monitored regularly to determine the peroxide content. Under no circumstances should diethyl ether be used with a peroxide content in excess of 50 ppm, as an explosion could result. Peroxide test strips manufactured by EM Laboratories (available from Scientific Products Company, Cat. No. P1126-8 and other suppliers) are recommended for this test. Procedures for removal of peroxides from diethyl ether are included in the instructions supplied with the peroxide test kit.

4.4 Waste disposal must be in accordance with RCRA and applicable state rules.

5.0 Apparatus and Materials

5.1 Sampling containers - Amber glass bottles, 1-L or other appropriate volume, fitted with screw caps lined with Teflon are appropriate for liquid samples. Cleaned foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, samples should be protected from light using foil or a light-tight outer container. The bottle must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination. Non-liquid samples may require other containers. Gas bags and stainless steel cannisters may be appropriate for gas samples. Bags or cans may be appropriate for solid samples. Consumer products in small containers may remain in the manufacturer's packaging.

5.2 Glassware - All specifications are suggestions only. Catalog numbers are included for illustration only.

5.2.1 Volumetric flasks - Assorted sizes.

5.2.2 Pipets - Assorted sizes, Mohr delivery.

5.2.3 Micro syringes - 10.0 µL for packed column GC analysis, 1.0 µL for on-column GC analysis.

5.2.4 Chromatographic column - Chromaflex, 400 mm long x 19 mm ID (Kontes K-420540-9011 or equivalent).

5.2.5 Kuderna-Danish Evaporative Concentrator Apparatus

5.2.5.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked. Ground glass stopper size (S19/22 joint) is used to prevent evaporation of solvent.

5.2.5.2 Evaporative flask - 500 mL (Kontes K-57001-0500 or equivalent). Attached to concentrator tube with springs (Kontes K-662750-0012 or equivalent).

5.2.5.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

5.3 Balance - Analytical, capable of accurately weighing 0.0001 g.

5.4 Gas chromatography/mass spectrometer system.

5.4.1 Gas chromatograph - An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port must be designed for on-column injection when using capillary columns or packed columns. Other capillary injection techniques (split, splitless, "Grob," etc.) may be used provided the performance specifications stated in Section 7.1 are met.

5.4.2 High resolution (capillary) GC column - A 10-30 m long x 0.25 mm ID fused silica column with a 0.25 µm thick DB-5 bonded silicone liquid phase (J&W Scientific) is recommended. Alternate liquid phases may include OV-101, SP-2100, Apiezon L, Dexsil 300, or other liquid phases or columns which meet the performance specifications stated in Section 7.1.

5.4.3 Packed GC column - A 180 cm x 0.2 cm ID glass column packed with 3% SP-2250 on 100/120 mesh Supelcoport or equivalent is recommended. Other liquid phases or columns which meet the performance specifications stated in Section 7.1 may be substituted.

5.4.4 Mass spectrometer - Must be capable of scanning from m/z 150 to m/z 550 every 1.5 sec or less, collecting at least five spectra per chromatographic peak, utilizing a 70-eV (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 2 when 50 ng of decafluorotriphenyl phosphine [DFTPP, bis(perfluorophenyl)phenyl phosphine] is injected through the GC inlet. Any GC-to-MS interface that gives acceptable calibration points at 10 ng per injection for each PCB isomer in the calibration standard and achieves all acceptable performance criteria (Section 10) may be used. Direct coupling of the fused silica column to the MS is recommended. Alternatively, GC-to-MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

5.4.5 A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The data system must have the capability of integrating the abundances of the selected ions between specified limits and relating integrated abundances to concentrations using the calibration procedures described in this method. The computer must have software that allows searching any GC/MS data file for ions of a specific mass

Table 2. DFTPP Key Ions and Ion Abundance Criteria

m/z	Ion abundance criteria
197	Less than 1% of mass 198
198	100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present, but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

and plotting such ion abundances versus time or scan number to yield an extracted ion current profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

5.5 Chromatographic systems.

5.5.1 Gel permeation chromatography.

5.5.1.1 GPC Autoprep 1002 (Analytical BioChemistry Laboratories, Inc.) or equivalent.

5.5.1.2 A Bio-Beads SX-3 (Bio-Rad) column.

5.5.2 High performance liquid chromatography.

5.5.2.1 Waters Model 6000A pump or equivalent.

5.5.2.2 Waters Model 440 UV detector or equivalent.

5.5.2.3 Rheodyne 7125 injector or equivalent.

5.5.2.4 Amine column (Waters μBondapak, 3.9 x 300 mm) or equivalent.

5.5.3 Gas chromatograph for GC/FID screening.

5.5.3.1 A temperature-programmable GC equipped with a flame ionization detector. Varian 3740 or equivalent.

5.5.3.2 A 2 m x 2 mm ID glass column packed with 3% SP-2250 on 100/120 mesh Supelcoport or equivalent. A high resolution GC column may also be used.

6.0 Reagents

6.1 Solvents - All solvents must be pesticide residue analysis grade. New lots should be checked for purity by concentrating an aliquot by at least as much as is used in the procedure. HPLC solvents should have UV cutoffs of 210 nm or less.

6.2 Calibration standard congeners - Standards of the PCB congeners listed in Tables 3 and 4 are available from Ultra Scientific, Hope, Rhode Island; or Analabs, North Haven, Connecticut.

Table 3. Concentrations of Congeners in PCB Calibration Standards for Full Scan Analysis (ng/μL)[a]

Homolog	Congener no.	FS100 ng PCB	FS050 ng PCB	FS010 ng PCB	FS005 ng PCB	FS001 ng PCB
1	1	100	50	10	5	1
2	7	100	50	10	5	1
3	30	150	75	15	7.5	1.5
4	50	200	100	20	10	2
5	97	200	100	20	10	2
6	143	200	100	20	10	2
7	183	300	150	30	15	3
8	202	300	150	30	15	3
9	207	450	225	45	22.5	4.5
10	209	200	100	20	10	2
4	210 (IS)	250	250	250	250	250
-	$C_{10}H_7I$ (IS)[b]	250	250	250	250	250
-	$C_{18}D_{12}$ (IS)[c]	250	250	250	250	250
^{13}C-Cl_1	211 (RS)	100	50	10	5	1
^{13}C-Cl_4	212 (RS)	250	125	25	12.5	2.5
^{13}C-Cl_8	213 (RS)	400	200	40	20	4
^{13}C-Cl_{10}	214 (RS)	500	250	50	25	5

[a] Concentrations given as examples only.
[b] 1-Iodonaphthalene.
[c] d_{12}-Chrysene.

Table 4. Concentrations of Congeners in PCB Calibration Standards for Selected Ion Monitoring and Limited Mass Scan Analysis (pg/μL)[a]

Homolog	Congener no.	SIM1000 pg PCB	SIM100 pg PCB	SIM050 pg PCB	SIM010 pg PCB
1	1	1,000	100	50	10
2	7	1,000	100	50	10
3	30	1,500	150	75	15
4	50	2,000	200	100	20
5	97	2,000	200	100	20
6	143	2,000	200	100	20
7	183	3,000	300	150	30
8	202	3,000	300	150	30
9	207	4,500	450	225	45
10	209	2,000	200	100	20
4	210 (IS)	250	250	250	250
-	$C_{10}H_7I$ (IS)[b]	250	250	250	250
-	$C_{18}D_{12}$ (IS)[c]	250	250	250	250
^{13}C-Cl_1	211 (RS)	1,000	100	50	10
^{13}C-Cl_4	212 (RS)	2,500	250	125	25
^{13}C-Cl_8	213 (RS)	4,000	400	200	40
^{13}C-Cl_{10}	214 (RS)	5,000	500	250	50

[a] Concentrations given as examples only.
[b] 1-Iodonaphthalene.
[c] d_{12}-Chrysene.

6.3 Calibration standard stock solutions - Primary dilutions of each of the individual PCBs listed in Tables 3 and 4 are prepared by weighing approximately 1-10 mg of material within 1% precision. The PCB is then dissolved and diluted to 1.0 mL with hexane. The concentration is calculated in mg/mL. The primary dilutions are stored at 4°C in screw-cap vials with Teflon cap liners. The meniscus is marked on the vial wall to monitor solvent evaporation. Primary dilutions are stable indefinitely if the seals are maintained. The stock solutions and dilutions should be clearly labeled with pertinent information such as sample code, solvent, date prepared, initials of person preparing the solution, and notebook reference.

6.4 Working calibration standards - Working calibration standards are prepared that are similar in PCB composition and concentration to the samples by mixing and diluting the individual standard stock solutions. Example calibration solutions are shown in Tables 3 and 4. The mixture is diluted to volume with pesticide residue analysis quality hexane. The concentration is calculated in ng/mL as the individual PCBs. Dilutions are stored at 4°C in narrow-mouth, screw-cap vials with Teflon cap liners. The meniscus is marked on the vial wall to monitor solvent evaporation. These secondary dilutions can be stored indefinitely if the seals are maintained.

These solutions are designated FSxxx ng PCB and SIMxxx pg PCB where the xxx is used to encode the nominal concentration of the lower congeners in ng/µL and pg/µL, respectively. The FS prefix helps aid the analyst in identifying solutions which are appropriate for full scan analysis; the SIM prefix is for solutions to calibrate in the selected ion monitoring and limited mass scan acquisition modes.

6.5 Alternatively, certified stock solutions similar to those listed in Tables 3 and 4 may be available from a supplier, in lieu of the procedure described in Section 6.4.

6.6 DFTPP standard - A 50-ng/µL solution of decafluorotriphenylphosphine (DFTPP, PCR Research Chemicals, Gainesville, FL) is prepared in acetone or another appropriate solvent.

6.7 Surrogate standard stock solution - The four ^{13}C-labeled PCBs listed in Table 5 are available as a certified solution from Toxic and Hazardous Materials Repository, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, 26 West St. Clair Street, Cincinnati, Ohio 45268, (513) 684-7327. This solution may be used as received or diluted further. These solutions are designated "SSxxx," where the xxx is used to encode the nominal concentration in µg/mL.

6.8 Internal standard solutions - Solutions of d_6-3,3',4,4'-tetrachlorobiphenyl (KOR Isotopes, Cambridge, MA), 1-iodonaphthalene (Aldrich Chemical Company, Milwaukee, WI) or d_{12}-chrysene (KOR

Table 5. Composition of Internal Standard Spiking Solution (SS100) Containing ^{13}C-Labeled PCBs

Congener no.	Compound	Abbreviations	Concentration (μg/mL)
211	4-Chloro-(1',2',3',4',5',6'-$^{13}C_6$)-biphenyl	^{13}C-Cl_1	100
212	3,3',4,4'-Tetrachloro-($^{13}C_{12}$)-biphenyl	^{13}C-Cl_4	250
213	2,2',3,3',5,5',6,6'-Octachloro-($^{13}C_{12}$)-biphenyl	^{13}C-Cl_8	400
214	Decachloro-($^{13}C_{12}$)-biphenyl	^{13}C-Cl_{10}	500

Isotopes, Cambridge, MA) are prepared at nominal concentrations of 1-10 mg/mL in hexane. The solutions are further diluted to give working standards.

Note: Any internal standard may be used, provided it meets the following criteria: (a) it is not already present in the sample, (b) it gives a strong, recognizable mass spectrum, (c) it does not give mass spectral ions which interfere with native or ^{13}C-labeled PCB quantitation, (d) it is chemically stable, and (e) it elutes in the PCB retention window. Ideally, several internal standards are used which have retention times spanning the PCB retention windows to improve the response factor precision.

6.9 Solution stability - The calibration standard, surrogate, and DFTPP solutions should be checked frequently for stability. These solutions should be replaced after 6 months, or sooner if comparison with quality control check samples indicates compound degradation or concentration change.

7.0 Calibration

7.1 The gas chromatograph must meet the minimum operating parameters shown in Tables 6 and 7, daily. If all criteria are not met, the analyst must adjust conditions and repeat the test until all criteria are met.

7.2 The mass spectrometer must meet the minimum operating parameters shown in Tables 2, 8, and 9, daily. If all criteria are not met, the analyst must retune the spectrometer and repeat the test until all conditions are met.

7.2.1 Full scan data acquisition - Quadrupole mass spectrometers must meet the tuning criteria in Table 2. The spectrometer must scan between m/z 150-550, although wider scan ranges are permissible.

7.2.2 Limited mass scan data acquisition - Table 10 presents a suggested set of LMS ranges. The mass spectrometer should be set to at least unit resolution. The computer acquisition parameters should utilize the minimum threshold filtering necessary so as not to lose pertinent data. Optimum acquisition parameters will vary depending on the condition of the mass spectrometer and should be checked daily.

Table 6. Operating Parameters for Capillary Column Gas Chromatographic System

Parameter	Recommended	Tolerance
Gas chromatograph	Finnigan 9610	Other[a]
Column	15 -30 m x 0.255 mm ID Fused silica	Other
Liquid phase	DB-5 (J&W)	Other nonpolar or semipolar
Liquid phase thickness	0.25 µm	< 1 µm
Carrier gas	Helium	Hydrogen
Carrier gas velocity	30-45 cm/s[b]	Optimum performance
Injector	"Grob" (split/splitless mode)[c]	Other[c]
Injector temperature	250-270°C	Optimum performance
Injection volume	1.0-2.0 µL	Other
Initial column temperature	60-80°C (2 min)[d]	Other[d]
Column temperature program	70°-300°C at 10°C/min[e]	Other
Separator	None[f]	Glass jet or other
Transfer line temperature	280°C	Optimum[g]
Tailing factor[h]	0.7-1.5	0.4-3
Peak width[i]	7-10 s	< 15 s

[a] Substitutions permitted with any common apparatus or technique provided performance criteria are met.
[b] Measured by injection of air or methane at 270°C oven temperature.
[c] Manufacturer's instructions should be followed regarding injection technique.
[d] With on-column injection, initial temperature equals boiling point of the solvent; in this instance, hexane.
[e] $C_{12}Cl_{10}$ elutes at 270°C. Programming above this temperature ensures a clean column and lower background on subsequent runs.
[f] Fused silica columns may be routed directly into the ion source to prevent separator discrimination and losses.
[g] High enough to elute all PCBs, but not high enough to degrade the column if routed through the transfer line.
[h] Tailing factor is width of front half of peak at 10% height divided by width of back half of peak at 10% height for single PCB congeners in solution FSxxx ng PCB or SIMxxx pg PCB.
[i] Peak width at 10% height for a single PCB congener in FSxxx ng PCB or SIMxxx pg PCB.

Table 7. Operating Parameters for Packed Column Gas Chromatography System

Parameter	Recommended	Tolerance
Gas chromatograph	Finnigan 9610	Other[a]
Column	180 cm x 0.2 cm ID glass	Other
Column packing	3% SP-2250 on 100/120 mesh Supelcoport	Other nonpolar or semipolar
Carrier gas	Helium	Hydrogen
Carrier gas flow rate	30 mL/min	Optimum performance
Injector	On-column	Other
Injector temperature	250°C	Optimum[b]
Injection volume	1.0 µL	≦ 5 µL
Initial column temperature	150°C, 4 min	Other
Column temperature program	150°-260°C at 8°/min	Other
Separator	Glass jet	Other
Transfer line temperature	280°C	Optimum[b]
Tailing factor[c]	0.7-1.5	0.4-3
Peak width[d]	10-20 sec	< 30 sec

[a]Substitutions permitted if performance criteria are met.
[b]High enough to elute all PCBs.
[c]Tailing factor is width of front half of peak at 10% height divided by width of back half of peak at 10% height for single PCB congeners in solution FSxxx ng PCB or SIMxxx pg PCB.
[d]Peak width at 10% height for a single PCB congener in FSxxx ng PCB or SIMxxx pg PCB.

Table 8. Operating Parameters for Quadrupole Mass Spectrometer System

Parameter	Recommended	Tolerance
Mass spectrometer	Finnigan 4023	Other[a]
Data system	Incos 2400	Other
Scan range	95-550	Other
Scan time	1 sec	Other[b]
Resolution	Unit	Optimum performance
Ion source temperature	280°C	200°-300°C
Electron energy[c]	70 eV	70 eV

[a]Substitutions permitted if performance criteria are met.
[b]Greater than five data points over a GC peak is a minimum.
[c]Filaments should be shut off during solvent elution to improve instrument stability and prolong filament life, especially if no solvent venting is used.

Table 9. Operating Parameters for Magnetic Sector Mass Spectrometer System

Parameter	Recommended	Tolerance
Mass spectrometer	Finnigan MAT 311A	Other[a]
Data system	Incos 2400	Other
Scan range	98-550	Other
Scan mode	Exponential	Other
Cycle time	1.2 sec	Other[b]
Resolution	1,000	> 500
Ion source temperature	280°C	250-300°
Electron energy[c]	70 eV	70 eV

[a]Substitutions permitted if performance criteria are met.
[b]Greater than five data points over a GC peak is a minimum.
[c]Filaments should be shut off during solvent elution to improve instrument stability and prolong filament life, especially if no solvent venting is used.

Table 10. Limited Mass Scanning (LMS) Ranges For PCBs

Compound	Mass range (m/z)
$C_{12}H_9Cl_1$ + $^{13}C_6{}^{12}C_6H_9Cl$	186-198
$C_{12}H_8Cl_2$	220-226
$C_{12}H_7Cl_3$	254-260
$C_{12}H_6Cl_4$ + $C_{12}D_6$ Cl_4 + $^{13}C_{12}H_6Cl_4$	288-310
$C_{12}H_5Cl_5$	322-328
$C_{12}H_4Cl_6$	356-362
$C_{12}H_3Cl_7$	390-396
$C_{12}H_2Cl_8$	426-434
$C_{12}HCl_9$	460-468
$C_{12}Cl_{10}$	496-502
$C_{10}H_7I$	254
$C_{18}D_{12}$	240
$^{13}C_{12}H_2Cl_8$	440-446
$^{13}C_{12}Cl_{10}$	508-514

The dwell times for the mass ranges given in Table 10 will vary with instrument and should be optimized to allow at least five data points across a chromatographic peak. Maximum sensitivity will be achieved when utilizing maximum dwell time.

Instruments having the capability to switch mass ranges during an analysis require particular attention to the switching points to assure minimal data loss. Switching points can be initially determined by analyzing a high level congener or Aroclor mixture while in the full scan mode.

7.2.3 Selected ion monitoring data acquisition - Table 11 presents a suggested set of characteristic ions for SIM. The SIM program must include at least two ions for each analyte, generally the primary and secondary ions in Table 11. The mass spectrometer should be set to at least unit resolution. The computer acquisition parameters should utilize the minimum threshold filtering necessary so as not to lose pertinent data. Optimum acquisition parameters will vary depending on the condition of the mass spectrometer and should be checked daily.

The dwell times for the masses given in Table 11 will vary with instrument and should be optimized to allow at least five data points across a chromatographic peak. Maximum sensitivity will be achieved when utilizing maximum dwell time.

Instruments having the capability to switch mass ranges during an analysis require particular attention to the switching points to assure minimal data loss. Switching points can be initially determined by analyzing a highly concentrated congener or Aroclor mixture while in the full scan mode.

7.3 The PCB response factors (RF_p) must be determined in triplicate or other replication, as discussed below, using Equation 7-1 for the analyte homologs.

$$RF_p = \frac{A_p \times M_{is}}{A_{is} \times M_p} \qquad \text{Eq. 7-1}$$

where RF_p = response factor of a given PCB congener

A_p = area of the characteristic ion for the PCB congener peak

M_p = mass of PCB congener in sample (micrograms)

Table 11. Characteristic SIM Ions for PCBs

Homolog	Ion (relative intensity)		
	Primary	Secondary	Tertiary
$C_{12}H_9Cl$	188 (100)	190 (33)	-
$C_{12}H_8Cl_2$	222 (100)	224 (66)	226 (11)
$C_{12}H_7Cl_3$	256 (100)	258 (99)	260 (33)
$C_{12}H_6Cl_4$	292 (100)	290 (76)	294 (49)
$C_{12}H_5Cl_5$	326 (100)	328 (66)	324 (61)
$C_{12}H_4Cl_6$	360 (100)	362 (82)	364 (36)
$C_{12}H_3Cl_7$	394 (100)	396 (98)	398 (54)
$C_{12}H_2Cl_8$	430 (100)	432 (66)	428 (87)
$C_{12}HCl_9$	464 (100)	466 (76)	462 (76)
$C_{12}Cl_{10}$	498 (100)	500 (87)	496 (68)
$C_{10}H_7I$	254 (100)	-	-
$C_{12}D_6Cl_4$	298 (100)	300 (49)	296 (76)
$C_{18}D_{12}$	240 (100)	-	-
$^{13}C_6{}^{12}C_6H_9Cl$	194 (100)	196 (33)	-
$^{13}C_{12}H_6Cl_4$	304 (100)	306 (49)	302 (76)
$^{13}C_{12}H_2Cl_8$	442 (100)	444 (65)	440 (87)
$^{13}C_{12}Cl_{10}$	510 (100)	512 (87)	508 (68)

A_{is} = area of the characteristic ion for the internal standard peak (d_6-3,3',4,4'-tetrachlorobiphenyl 1-iodonaphthalene or other compound)

M_{is} = mass of internal standard in sample (micrograms)

Using the same conditions as for RF_p, the surrogate response factors (RF_s) must be determined using Equation 7-2.

$$RF_s = \frac{A_s \times M_{is}}{A_{is} \times M_s} \qquad \text{Eq. 7-2}$$

where A_s = area of the characteristic ion for the surrogate peak

M_s = mass of surrogate in sample (micrograms)

Other terms are the same as defined in Equation 7-1.

If specific congeners are known to be present and if standards are available, selected RF values may be employed. For general samples, solutions in Tables 3 and 4 or a mixture with a similar level of internal standard added, may be used as the response factor solution. The PCB-surrogate pairs to be used in the RF calculation are listed in Table 12.

Generally, only the primary ions of both the analyte and surrogate are used to determine the RF values. If alternate ions are to be used in the quantitation, the RF must be determined using that characteristic ion.

The RF value must be determined in a manner to assure ± 20% precision. For instruments with good day-to-day precision, a running mean ($\overline{RF}$) based on seven values may be appropriate. A new value is added each day and the oldest dropped from the mean. Other options include, but are not limited to, triplicate determinations of a single concentration spaced throughout a day or determination of the RF at three different levels to establish a working curve. If samples are being analyzed on successive days, a single RF determination which is within ± 20% of the initial day's triplicate determination may be used.

If replicate RF values differ by greater than ± 10% RSD, the system performance should be monitored closely. If the RSD is greater than ± 20%, the data set must be considered invalid and the RF redetermined before further analyses are done. The analyst is responsible for maintaining records of the RF precision.

Table 12. Pairings of Analyte and Calibration Compounds

Analyte		Calibration standard	
Congener[a] no.	Compound	Congener no.	Compound
1-3	$C_{12}H_9Cl$	1	2
4-15	$C_{12}H_8Cl_2$	7	2,4
16-39	$C_{12}H_7Cl_3$	30	2,4,6
40-81	$C_{12}H_6Cl_4$	50	2,2',4,6
82-127	$C_{12}H_5Cl_5$	97	2,2',3',4,5
128-169	$C_{12}H_4Cl_6$	143	2,2',3,4,5,6'
170-193	$C_{12}H_3Cl_7$	183	2,2',3',4,4',5',6
194-205	$C_{12}H_2Cl_8$	202	2,2',3,3',5,5',6,6'
206-208	$C_{12}HCl_9$	207	2,2',3,3',4,4',5,6,6'
209	$C_{12}Cl_{10}$	209	$C_{12}Cl_{10}$

[a]Ballschmiter numbering system, see Table 1.

7.4 If the GC/EIMS system has not been demonstrated to yield a linear response or if the analyte concentrations are more than two orders of magnitude different from those in the RF solution, a calibration curve must be prepared. If the analyte and RF solution concentrations differ by more than one order of magnitude, a calibration curve should be prepared. A calibration curve should be established with triplicate determinations at three or more concentrations bracketing the analyte levels.

7.5 The relative retention time (RRT) windows for the 10 homologs and surrogates must be determined unless the entire chromatogram is scanned for each homolog. If all congeners are not available, a mixture of available congeners or an Aroclor mixture (e.g., 1016/1254/1260) may be used to estimate the windows. The windows must be set wider than observed if all isomers are not determined. Typical RRT windows for one column are listed in Table 13. The windows may differ substantially if other GC parameters are used.

8.0 Sample Collection, Handling, and Preservation

8.1 Amber glass sample containers should have Teflon-lined screw caps. With noncorrosive samples, methylene chloride-washed aluminum foil liners may be substituted. The volume and configuration are determined by the amount of sample to be collected and its physical properties. For dry powders, other containers such as wide-mouthed ointment jars or heavy-walled polyethylene bags may be appropriate.

8.2 Sample bottle preparation

8.2.1 All sample containers and caps should be washed in detergent solution, rinsed with tap water, and then with distilled water. The bottles and caps are allowed to drain dry in a contaminant-free area. Then the caps are rinsed with pesticide grade hexane and allowed to air dry.

8.2.2 Sample bottles are heated to 400°C for 15 to 20 min or rinsed with pesticide grade acetone or hexane and allowed to air dry.

8.2.3 The clean bottles are stored inverted and sealed until use.

8.3 Sample collection - Sample collection must be designed to meet sampling objectives.

8.3.1 The primary consideration in sample collection is that the sample collected be representative of the whole. Therefore, sampling plans or protocols for each individual producer's situation will have to be developed. The recommendations presented here describe general situations. The number of replicates and sampling frequency also must be planned prior to sampling.

Table 13. Relative Retention Time (RRT) Ranges of PCB Homologs Versus d_6-3,3',4,4'-Tetrachlorobiphenyl

PCB homolog	No. of isomers measured	Observed range of RRTs[a]	Congener no.	Observed RRT[a]	Projected range of RRTs[b]
Monochloro	3	0.40-0.50	1	0.43	0.35-0.55
Dichloro	10	0.52-0.69	7	0.58	0.45-0.80
Trichloro	9	0.62-0.79	30	0.65	0.55-1.00
Tetrachloro	16	0.72-1.01	50	0.75	0.55-1.05
Pentachloro	12	0.82-1.08	97	0.98	0.80-1.10
Hexachloro	13	0.93-1.20	143	1.05	0.90-1.25
Heptachloro	4	1.09-1.30	183	1.15	1.05-1.35
Octachloro	6	1.19-1.36	202	1.19	1.10-1.50
Nonachloro	3	1.31-1.42	207	1.33	1.25-1.50
Decachloro	1	1.44-1.45	209	1.44	1.35-1.50

[a]The RRTs of the 77 congeners and a mixture of Aroclor 1016/1254/1260 were measured versus 3,3',4,4'-tetrachlorobiphenyl-d_6 (internal standard) using a 15-m J&W DB-5 fused silica column with a temperature program of 110°C for 2 min, then 10°C/min to 325°C, helium carrier at 45 cm/sec, and an on-column injector. A Finnigan 4023 Incos quadrupole mass spectrometer operating with a scan range of 95-550 daltons was used to detect each PCB congener.

[b]The projected relative retention windows account for overlap of eluting homologs and take into consideration differences in operating systems and lack of all possible 209 PCB congeners.

8.3.2 Discrete product units - If the product is small enough that one or more discrete units would be used as the analytical sample, a statistically random sampling approach is recommended.

8.3.3 Liquids or free-flowing solids - If possible, the source is mixed thoroughly before collecting the sample. If mixing is impractical, the sample should be collected from a representative area of the source. If the liquid is flowing through an enclosed system, sampling through a valve should be randomly timed.

8.3.4 Solids - Larger bulk solids which must be subsampled to get a reasonably sized analytical sample must be treated on a case-by-case basis. A representative sample should be obtained by designing a sampling location selection scheme such that all parts of the whole have a finite, known probability of inclusion. Based on such a scheme, the PCB content of the sample can be used to extrapolate to the content of the whole.

8.4 Sample preservation - Product samples should be stored as the bulk or packaged product inventory would be stored, or in a cool, dry, dark area. Intermediates, process samples, or other non-product specimens should be stored at 4°C. If there is a possibility of microbial degradation, addition of H_2SO_4 during collection to a pH < 2 is recommended. A test strip is used to monitor pH. Storage times in excess of 4 weeks are not recommended.

If residual chlorine is present in the sample, it should be quenched with sodium thiosulfate. EPA Methods 330.4 and 330.5 may be used to measure the residual chlorine.[6] Field test kits are available for this purpose.

9.0 Sample Preparation

Since a wide variety of matrices may be subjected to analysis by this method, the extraction/cleanup procedure cannot be specified. This section describes general guidelines for subsampling, addition of ^{13}C surrogates, dilution, extraction, cleanup, extract concentration, and other sample preparation procedures.

9.1 Sample homogenization and subsampling - The sample is homogenized by shaking, blending, shredding, crushing, or other appropriate mechanical technique. A representative subsample of 100 g or other known mass is then taken. The sample size is dependent upon the anticipated PCB levels and difficulty of the subsequent extraction/cleanup steps.

Note: The precision of the mass determination at this step will be reflected in the overall method precision. Therefore, an analytical balance must be used to assure that the weight is accurate to ± 1% or better.

9.2 Surrogate addition - An appropriate volume of surrogate solution SSxxx must be pipetted into the sample. The final concentration of the surrogates must be in the working range of the calibration and well above the matrix background. The surrogates are thoroughly incorporated by further mechanical agitation. For nonviscous liquids, shaking for 30 sec should be sufficient. For viscous liquids or free-flowing solids, 10-min tumbling is recommended. In cases where inadequate incorporation may be expected, such as solids, overnight equilibration with agitation is recommended.

Note: The volume measurement of the spiking solution is critical to the overall method precision. The analyst must exercise caution that the volume is known to ± 1% or better. Where necessary, calibration of the pipet is recommended.

9.3 Sample preparation (extraction/cleanup) - After addition of the surrogates, the sample is further treated at the discretion of the analyst, provided that the GC/EIMS response of the four surrogates are sufficient for reliable quantitation. The literature pertaining to these techniques has been reviewed.[5] Several possible techniques are presented below for guidance only. The applicability of any of these techniques to a specific sample matrix must be determined by the precision and accuracy of the ^{13}C PCB surrogate recoveries, as discussed in Section 15.4.1.

9.3.1 Extraction

9.3.1.1 Dilution - In some cases, where the PCB concentration is high, a simple volumetric dilution with an appropriate solvent may be sufficient sample preparation.

9.3.1.2 Direct injection - If sample viscosity permits, direct injection with no dilution is permissible.

9.3.1.3 Kuderna-Danish concentration - If the sample is a solvent with low PCB concentration, reduction of sample volume may be sufficient preparation. In this case, the sample is placed in the Kuderna-Danish apparatus and concentrated over steam to an appropriate volume. (Alternatives to Kuderna-Danish, such as rotary evaporation techniques may also be used.)

9.3.1.4 Evaporative concentration using nitrogen - For smaller volume (5-50 mL) solvent samples concentration may be achieved by blowing sample with

a gentle stream of pre-purified nitrogen. Concentrate sample to final volume, rinse sides of vial with small aliquots of solvent, and again concentrate to final volume. In some cases, where background is a problem, concentration to dryness will eliminate interference by low-boiling compounds, e.g., chloroform, without removing the more volatile PCBs. After blowing to dryness, reconstitute with solvent and sonicate for 5 min. Care must be taken to avoid evaporative loss of the more volatile PCBs. Do not heat a dry sample for extended periods.

9.3.1.5 Liquid-liquid extraction - If the matrix is aqueous (or another solvent in which PCBs are only slightly soluble), a liquid-liquid partition may be effective. The solvent, number of extractions, solvent-to-sample ratio, and other parameters are chosen at the analyst's discretion.

9.3.1.6 Sorbent column extraction - PCBs may be isolated from free-flowing liquids onto sorbent columns. The selection of sorbent (XAD, Porapak, carbon-polyurethane foam, etc.) will depend on the nature of the matrix. The available methods have been reviewed.[5]

9.3.1.7 Thermal desorption - If the matrix is nonvolatile, thermal desorption of the PCBs onto a sorbent column, filter, or cold trap may be an effective extraction/cleanup method.

9.3.1.8 Matrix destruction - Some matrices may be easily degraded to a volatile or extractable compound. Once the matrix is degraded, the PCBs can be isolated, either by evaporation of the matrix or partitions of the PCBs into a nonpolar solvent and the matrix into a polar solvent (e.g., water). Examples include: (1) esters which may be saponified with base to the acid anion and then extracted with water, and (2) acid chlorides which may be hydrolyzed to the acid anion with water or base and then extracted with water.

9.3.2 Cleanup - Several tested cleanup techniques are described below. All but the base cleanup (9.3.2.8) were previously validated for PCBs in transformer fluids.[7] Depending upon the complexity of the sample, one or more of the techniques may be required to fractionate the PCBs from interferences. For most cleanups a concentrated (1-5 mL) extract should be used.

9.3.2.1 Acid cleanup

9.3.2.1.1 Place 5 mL of concentrated sulfuric acid into a 40-mL narrow-mouth screw-cap bottle. Add the sample extract. Seal the bottle with a Teflon-lined screw cap and shake for 1 min.

9.3.2.1.2 Allow the phases to separate, transfer the sample (upper phase) with three rinses of 1-2 mL solvent to a clean container.

9.3.2.1.3 Back-extract sample extract with 5-10 drops of distilled water. Pass through a short column of anhydrous sodium sulfate and concentrate to an appropriate volume.

9.3.2.1.4 Analyze as described in Section 10.0.

9.3.2.1.5 If the sample is highly contaminated, a second or third acid cleanup may be employed.

9.3.2.2 Florisil column cleanup

9.3.2.2.1 Variations among batches of Florisil (PR grade or equivalent) may affect the elution volume of the various PCBs. For this reason, the volume of solvent required to completely elute all PCBs must be verified by the analyst. The weight of Florisil can then be adjusted accordingly.

9.3.2.2.2 Place a 20-g charge of Florisil, activated overnight at 130°C, into a Chromaflex column. Settle the Florisil by tapping the column. Add about 1 cm of anhydrous sodium sulfate to the top of the Florisil. Pre-elute the column with 70-80 mL of hexane. Just before the exposure of the sodium sulfate layer to air, stop the flow. Discard the eluate.

9.3.2.2.3 Add the sample extract to the column.

9.3.2.2.4 Carefully wash down the inner wall of the column with 5 mL of hexane.

9.3.2.2.5 Add 200 mL of 6% ethyl ether/hexane and set the flow to about 5 mL/min.

9.3.2.2.6 Collect 200 mL of eluate in a Kuderna-Danish flask. All the PCBs should be in this fraction. Concentrate to an appropriate volume.

9.3.2.2.7 Analyze the sample as described in Section 10.0.

9.3.2.3 Alumina column cleanup

9.3.2.3.1 Adjust the activity of the alumina (Fisher A540 or equivalent) by heating to 200°C for at least 2 hr. When cool, add 3% water (wt:wt) and mix until uniform. Allow the deactivated alumina to equilibrate at least 1/2 hr before use. Store in a tightly sealed bottle.

9.3.2.3.2 Variations between batches of alumina may affect the elution volume of the various PCBs. For this reason, the volume of solvent required to completely elute all of the PCBs must be verified by the analyst. The weight of alumina can then be adjusted accordingly.

9.3.2.3.3 Place a 50-g charge of alumina into a Chromaflex column. Settle the alumina by tapping. Add about 1 cm of anhydrous sodium sulfate. Preelute the column with 70-80 mL of hexane. Just before exposure of the sodium sulfate layer to air, stop the flow. Discard the eluate.

9.3.2.3.4 Add the sample extract to the column.

9.3.2.3.5 Carefully wash down the inner wall of the column with 5 mL of hexane.

9.3.2.3.6 Add 295 mL of hexane to the column.

9.3.2.3.7 Discard the first 50 mL.

9.3.2.3.8 Collect 250 mL of the hexane in a Kuderna-Danish flask. All of the PCBs should be in this fraction. Concentrate to an appropriate volume.

9.3.2.3.9 Analyze the sample as described in Section 10.0.

9.3.2.4 Silica gel column cleanup

9.3.2.4.1 Activate silica gel (Davison Grade 950 or equivalent) at 135°C overnight.

9.3.2.4.2 Variations between batches of silica gel may affect the elution volume of the various PCBs. For this reason, the volume of solvent required to completely elute all of the PCBs must be verified by the analyst. The weight of silica gel can then be adjusted accordingly.

9.3.2.4.3 Place a 25-g charge of activated silica gel into a Chromaflex column. Settle the silica gel by tapping the column. Add about 1 cm of anhydrous sodium sulfate to the top of the silica gel.

9.3.2.4.4 Pre-elute the column with 70-80 mL of hexane. Discard the eluate. Just before exposing the sodium sulfate layer to air, stop the flow.

9.3.2.4.5 Add the sample extract to the column.

9.3.2.4.6 Wash down the inner wall of the column with 5 mL of hexane.

9.3.2.4.7 Elute the PCBs with 195 mL of 10% diethyl ether in hexane (v:v).

9.3.2.4.8 Collect 200 mL of the eluate in a Kuderna-Danish flask. All of the PCBs should be in this fraction. Concentrate to an appropriate volume.

9.3.2.4.9 Analyze the sample as described in Section 10.0.

9.3.2.5 Gel permeation cleanup

9.3.2.5.1 Set up and calibrate the gel permeation chromatograph with an SX-3 column according to the Autoprep instruction manual. Use 15% methylene chloride in cyclohexane (v:v) as the mobile phase.

9.3.2.5.2 Inject 5.0 mL of the sample extract into the instrument. Collect the fraction containing the PCBs (see Autoprep operator's manual) in a Kuderna-Danish flask equipped with a 10-mL ampul.

9.3.2.5.3 Concentrate the PCB fraction to an appropriate volume.

9.3.2.5.4 Analyze the sample as described in Section 10.0.

9.3.2.6 Acetonitrile partition

9.3.2.6.1 Place the sample extract into a 125-mL separatory funnel with enough hexane to bring the final volume to 15 mL. Extract the sample four times by shaking vigorously for 1 min with 30-mL portions of hexane-saturated acetonitrile. Retain hexane layer for combination with other hexane extracts in 9.3.2.6.3.

9.3.2.6.2 Combine and transfer the acetonitrile phases to a 1-L separatory funnel and add 650 mL of distilled water and 40 mL of saturated sodium chloride solution. Mix thoroughly for about 30 sec. Extract with two 100-mL portions of hexane by vigorously shaking about 15 sec.

9.3.2.6.3 Combine the hexane extracts in a 1-L separatory funnel and wash with two 100-mL portions of distilled water. Discard the water layer and pour the hexane layer through an 8- to 10-cm anhydrous sodium sulfate column into a 500-mL Kuderna-Danish flask equipped with a 10-mL ampul. Rinse the separatory funnel and column with three 10-mL portions of hexane.

9.3.2.6.4 Concentrate the extracts to an appropriate volume.

9.3.2.6.5 Analyze as described in Section 10.0.

9.3.2.7 Florisil slurry cleanup

9.3.2.7.1 Place the sample extract into a 20-mL narrow-mouth screw-cap container. Add 0.25 g of Florisil (PR grade or equivalent). Seal with a Teflon-lined screw cap and shake for 1 min.

9.3.2.7.2 Allow the Florisil to settle; then decant the treated solution into a second container with rinsing. Concentrate the sample to an appropriate volume. Analyze as described in Section 10.0.

9.3.2.8 Base cleanup[8]

9.3.2.8.1 Quantitatively transfer the concentrated extract to a 125-mL extraction flask with the aid of several small portions of solvent.

9.3.2.8.2 Evaporate the extract just to dryness with a gentle stream of dry filtered nitrogen, and add 25 mL of 2.5% alcoholic KOH.

9.3.2.8.3 Add a boiling chip, put a water condenser in place, and allow the solution to reflux on a hot plate for 45 min.

9.3.2.8.4 After cooling, transfer the solution to a 250-mL separatory funnel with 25 mL of distilled water.

9.3.2.8.5 Rinse the extraction flask with 25 mL of hexane and add it to the separatory funnel.

9.3.2.8.6 Stopper the separatory funnel and shake vigorously for at least 1 min. Allow the layers to separate, and transfer the lower aqueous phase to a second separatory funnel.

9.3.2.8.7 Extract the saponification solution with a second 25-mL portion of hexane. After the layers have separated, add the first hexane extract to the second separatory funnel and transfer the aqueous alcohol layer to the original separatory funnel.

9.3.2.8.8 Repeat the extraction with a third 25-mL portion of hexane. Discard the saponification solution, and combine the hexane extracts.

9.3.2.8.9 Concentrate the hexane layer to an appropriate volume, and analyze as described in Section 10.0.

9.3.2.9 High performance liquid chromatographic cleanup

9.3.2.9.1 Quantitatively transfer the concentrated extract into the sample loop or the barrel of a syringe. Rinse the vial with several small portions of solvent. It may be necessary to inject several fractions.

9.3.2.9.2 Inject the extract and washes onto the amine column (Waters μBondapak 3.9 x 300 mm or equivalent) and elute the PCBs with 1.0 mL/min hexane. The UV at 254 nm or lower should be monitored.

9.3.2.9.3 Collect the eluent from 3 min to 9.5 min as it exits UV cell. The elution time should be verified using PCB standards covering a range from monochlorobiphenyls to decachlorobiphenyls.

9.3.2.9.4 After collection, wash the column by eluting with methylene chloride until the absorbance attains a stable minimum. Return the system to hexane.

9.3.2.9.5 Concentrate the hexane eluate under a gentle stream of purified nitrogen to an appropriate volume and analyze as described in Section 10.0.

9.4 Optional screening for interferences using GC/FID

Note: Since many sample matrices are one of a kind or infrequently encountered by the analyst, the effectiveness of the extraction and cleanup for a matrix may be unknown. A simple screen to assess whether the interferences have been reduced to a tolerable level can both save GC/MS time and prevent contamination of the GC/MS instrument with very dirty samples. This screen should <u>not</u> be used to determine PCB levels under this analytical method.

9.4.1 Using a GC system as described in Section 5.5.3, analyze for background interferences.

9.4.2 A 2 m x 2 mm glass column packed with 3% SP-2250 on 100/120 Supelcoport or equivalent is suggested. A flow rate of 40 mL/min 95% air/5% methane or nitrogen is recommended. The air and hydrogen flow rates should be sufficient to keep the flame lit and to burn efficiently, e.g., 300 mL/min air and 30 mL/min H_2.

9.4.3 The recommended temperature program is from 50°C to 250°C at 20°C/min with an initial hold of 3 min and a final hold of 10 min. The injector temperature should be 200°C and the detector 300°C.

9.4.4 Set instrumental sensitivity comparable to the anticipated mass spectral sensitivity. It is advisable to establish criteria for rejection of samples at a given attenuation such as (1) any off-scale peaks in PCB elution window, (2) a baseline rise of over 40% full-scale, and (3) other criteria which are indicative of "problem" samples.

9.4.5 If the FID screen suggests that the sample is not amenable to analysis by GC/EIMS, the analyst may either (1) cycle the sample through the same cleanup again if it appears that the cleanup technique was overloaded by the matrix the first time, (2) submit the extract to another cleanup technique which may remove more interferences, or (3) analyze a new aliquot of sample by another extraction or cleanup technique.

10.0 Gas Chromatographic/Electron Impact Mass Spectrometric Determination

10.1 Internal standard addition - An appropriate volume of the internal standard solution is pipetted into the sample. The final concentration of the internal standard must be in the working range of the calibration and well above the matrix background. The internal standard is thoroughly incorporated by mechanical agitation.

Note: The volumetric measurement of the internal standard solution is critical to the overall method precision. The analyst must exercise caution that the volume is known to be ± 1% or better. Where necessary, calibration of the pipet is recommended.

10.2 Tables 2, and 6 through 11 summarize the recommended operating conditions for analysis. Figure 1 presents an example of a chromatogram.

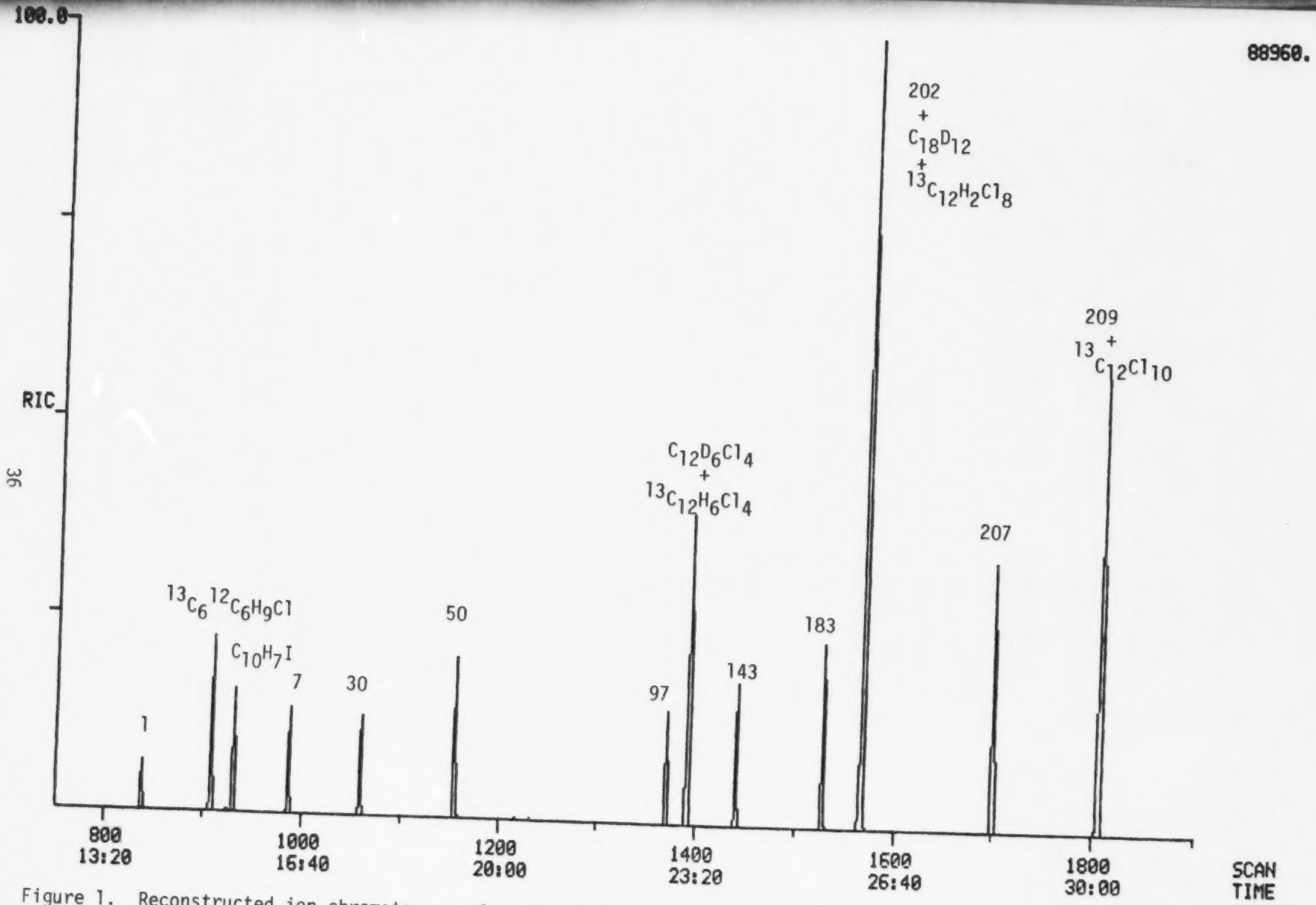

Figure 1. Reconstructed ion chromatogram of calibration solution FS100 ng PCB obtained in the full scan mode. The concentration of the 10 PCB calibration congeners, the four ^{13}C-labeled PCB recovery surrogates, and the three internal standards are in Table 3. See Table 1 for PCB numbering system, Table 6 for capillary GC parameters, and Table 8 for mass spectrometer operating parameters.

The analyst may choose to operate the mass spectrometer at any appropriate sensitivity, using either full scan, limited mass scanning or selected ion monitoring acquisition. The sensitivity selected will depend on anticipated PCB levels and the instrumental LOQ needed to meet the required method LOQ. In general, the more concentrated the PCBs, the greater the precision, accuracy, and qualitative data confidence. Thus, if possible, the amount of sample and the concentration factor should be scaled so that full scan acquisition may be utilized.

10.3 While the highest available chromatographic resolution is not a necessary objective of this method, good chromatographic performance is recommended. With the high resolution of HRGC, the probability that the chromatographic peaks consist of single compounds is higher than with PGC. Thus, qualitative and quantitative data reduction should be more reliable.

10.4 After performance of the system has been certified for the day and all instrument conditions set according to Tables 2, and 6 through 11, inject an aliquot of the sample onto the GC column. If the response for any ion, including surrogates and internal standards, exceeds the working range of the system, dilute the sample and reanalyze. If the responses of surrogates, internal standards, or analytes are below the working range, recheck the system performance. If necessary, concentrate the sample and reanalyze.

10.5 Record all data on a digital storage device (magnetic disk, tape, etc.) for qualitative and quantitative data reduction as discussed below.

10.6 The instrumental performance must be monitored from run-to-run. The areas of internal standards must be consistent (e.g., ± 20%). If a low area is encountered, the injection may be suspect.

The resolution and peak shape of the internal standards, surrogates, and other peaks should be monitored during or immediately after data acquisition. Poor chromatography may indicate a bad injection, matrix interferences, or column degradation.

10.7 If a "dirty" sample is encountered, the analyst must employ appropriate measures to demonstrate that there is no memory or carryons to subsequent samples. To assess the system cleanliness, a standard, blank sample, or solvent blank may be run.

If the system is contaminated, remedial efforts may include (1) changing or cleaning the syringe, (2) cleaning the injector, (3) baking out the column at its maximum temperature, (4) changing to a new column, or (5) cleaning the ion source.

11.0 Qualitative Identification

11.1 Full scan data

11.1.1 The peak must elute within the retention time windows set for that homolog (as described in Section 7.5).

11.1.2 The unknown spectrum should be compared to that of an authentic PCB. The intensity of the three largest ions in the molecular cluster (two largest for monochlorobiphenyls) must match the ratio observed for a standard within ± 20%. Fragment clusters with proper intensity ratios should also be present. System noise at low concentration or interferences may skew the ion ratio beyond the ± 20% criteria. If the analyst's best judgement is that a peak, which does not meet the qualitative criteria, is a PCB, the peak may be included in the calculation, with a footnote explaining the data and the reason for relaxing the criteria.

11.1.3 Alternatively, a spectral search may be used to automatically reduce the data. The criteria for acceptable identification include a high index of similarity.

11.2 Selected ion monitoring (SIM) or limited mass scan (LMS) data - The identification of a compound as a given PCB homolog requires that two criteria be met:

11.2.1 (1) The peak must elute within the retention time window set for that homolog (Section 7.5); and (2) the ratio of two ions obtained by LMS (Table 10) or by SIM (Table 11) must match the ratio observed for a standard within ± 20%. The analyst should search the higher mass windows, in particular M+70, to prevent misidentification of a PCB fragment ion cluster as the parent. System noise at low concentration or interferences may skew the ion ratio beyond the ± 20% criteria. If the analyst's best judgement is that a peak, which does not meet the qualitative criteria, is a PCB, the peak may be included in the calculation, with a footnote explaining the data and the reason for relaxing the criteria.

11.2.2 If one or the other of these criteria is not met, interferences may have affected the results, and a reanalysis using full scan EIMS conditions is recommended.

11.3 Disputes in interpretation - Where there is reasonable doubt as to the identity of a peak as a PCB, the analyst must either identify the peak as a PCB or proceed to a confirmational analysis (see Section 13.0).

12.0 Quantitative Data Reduction

12.1 After a chromatographic peak has been identified as a PCB, the compound is quantitated based on the integrated abundance of either the EICP or the SIM data for the primary characteristic ion in Tables 10 and 11. If interferences are observed for the primary ion, use the secondary and then tertiary ion for quantitation. If interferences in the parent cluster prevent quantitation, an ion from a fragment cluster (e.g., M-70) may be used. Whichever ion is used, the RF must be determined using that ion. The same criteria should be applied to the surrogate compounds (Table 14).

Note: With the higher homologs, the mass defect from unity is significant. For instance, the mass of the most intense peak for decachlorobiphenyl is 497.6830. Areas, EICPs, etc. must be based on the true mass, not the nominal mass, or erroneous results may be obtained. In addition, the tuning of some quadrupoles may be less stable at high masses. The data quality must be monitored especially carefully for the higher homologs.

12.2 Using the appropriate analyte-internal standard pair and response factor (RF_p) as determined in Section 7.3, calculate the concentration of each peak using Equation 12-1.

$$\text{Concentration } (\mu g/g) = \frac{A_p}{A_{is}} \cdot \frac{1}{RF_p} \cdot \frac{M_{is}}{M_e} \qquad \text{Eq. 12-1}$$

where A_p = area of the characteristic ion for the analyte PCB peak

A_{is} = area of the characteristic ion for the internal standard peak

RF_p = response factor of a given PCB congener

M_{is} = mass of internal standard added to sample extract (micrograms)

M_e = mass of sample extracted (grams)

12.3 If a peak appears to contain non-PCB interferences, which cannot be circumvented by a secondary or tertiary ion, either:

12.3.1 Reanalyze the sample on a different column which separates the PCB and interferents;

12.3.2 Perform additional chemical cleanup (Section 9) and then reanalyze the sample; or

12.3.3 Quantitate the entire peak as PCB.

Table 14. Characteristic Ions for Internal Standards and ^{13}C-Labeled PCB Surrogates

Compound	Abbreviation	Ion (relative intensity)		
		Primary	Secondary	Tertiary
d_6-3,4,3',4'-Tetrachlorobiphenyl	d_6-Cl_4	298 (100)	300 (49)	296 (78)
1-Iodonaphthalene	INAP	254	127	-
d_{12}-Chrysene	DCRY	240	-	-
$^{13}C_6{}^{12}C_6H_9Cl$	^{13}C-Cl_1	194 (100)	196 (33)	-
$^{13}C_{12}H_6Cl_4$	^{13}C-Cl_4	304 (100)	306 (49)	302 (78)
$^{13}C_{12}H_2Cl_8$	^{13}C-Cl_8	442 (100)	444 (65)	440 (89)
$^{13}C_{12}Cl_{10}$	^{13}C-Cl_{10}	510 (100)	512 (87)	514 (50)

12.4 Calculate the recovery of the four ^{13}C surrogates using the appropriate surrogate-internal standard pair and response factor (RF_{is}) as determined in Section 7.4 using Equation 12-2.

$$\text{Recovery (\%)} = \frac{A_s}{A_{is}} \cdot \frac{1}{RF_s} \cdot \frac{M_{is}}{M_s} \cdot 100 \qquad \text{Eq. 12-2}$$

where A_s = area of the characteristic ion for the surrogate peak

RF_s = response factor for the surrogate compound with respect to the internal standard (Equation 7-2)

M_s = mass of surrogate added to original sample (micrograms)

Other terms are the same as defined in Equation 12.1.

12.5 Sum all of the peaks for each homolog, and then sum those to yield the total PCB concentration in the sample. Report all numbers in µg/g. The worksheet in Table 15 and reporting form in Table 16 may be used. The concentrations and percent recovery of the four surrogates are to be reported.

If an alternate reporting format (e.g., concentration per peak) is desired, a different report form may be used. For example, if the PCB analysis is being conducted to satisfy regulatory requirements for by-product PCBs, results may need be reported on a per resolvable chromatographic peak basis. One rule[1] states that PCBs in products or wastes must be below the practical limit of quantitation, defined as "2 micrograms per gram (2 ppm) per resolvable chromatographic peak." For regulatory purposes, only peaks greater than the 2 µg/g cutoff may need to be reported. A second rule[2] requires reporting total PCBs, with a regulatory cutoff at an annual average of 25 ppm with a 50 ppm maximum.

12.6 Round off all numbers reported to two significant figures.

13.0 Confirmation

If there is significant reason to question the qualitative identification (Section 11), the analyst may choose to confirm that a peak is not a PCB. Any technique may be chosen provided that it is validated as having equivalent or superior selectivity and sensitivity to GC/EIMS. Some candidate techniques include alternate GC columns (with EIMS detection), GC/CIMS, GC/NCIMS, high resolution EIMS, and MS/MS techniques. Each laboratory must validate confirmation techniques to show equivalent or superior selectivity between PCBs and interferences and sensitivity (limit of quantitation, LOQ).

Table 15. Analysis Worksheet

BY-PRODUCT PCBs IN COMMERCIAL PRODUCTS OR PRODUCT WASTES

Internal Sample No. _____ External Sample No. _____
Notebook No. _____ Date Prepared _____
Data File Code _____ Date Analyzed _____

Amount Extracted _____ g Final Volume _____ mL

Internal standards	Conc. (µg/g)	Quant. ion	Ratio	Scan no.	Area	Check std. to be used for calculations
d_6Cl_4		298,300	100/49			☐
INAP		254				☐
DCRY		240				☐

Surrogate compounds	Conc. (µg/g)	Ions	Ratio	Scan no.	Area	% Recovery
$^{13}C\text{-}Cl_1$	194,196	100/33				
$^{13}C\text{-}Cl_4$	304,306	100/49				
$^{13}C\text{-}Cl_8$	442,444	100/65				
$^{13}C\text{-}Cl_{10}$	510,512	100/87				

Analyte homolog	Ions	Ratio
1-Cl	188,190	100/33
2-Cl	222,224	100/66
3-Cl	256,258	100/99
4-Cl	292,290	100/76
5-Cl	326,328	100/66

Analyte homolog	Ions	Ratio
6-Cl	360,362	100/82
7-Cl	394,396	100/98
8-Cl	430,432	100/66
9-Cl	464,466	100/76
10-Cl	498,500	100/87

Homolog	Scan no.(s)	Area(s)	Ratio	Total area	Ion used	RF	Conc. (µg/g)

Table 15 (continued)

BY-PRODUCT PCBs IN COMMERCIAL PRODUCTS OR PRODUCT WASTES

Internal Sample No. _____ External Sample No. _____
Data File Code _____

Homolog	Scan no.(s)	Area(s)	Ratio	Total area	Ion used	RF	Conc. (µg/g)

Table 16. Analysis Report

BY-PRODUCT PCBs IN COMMERCIAL PRODUCTS OR PRODUCT WASTES

Internal Sample No. _____ External Sample No. _____
Notebook No. _____ Sample Source _____
Data File Code _____ Sample Matrix _____

Amount Extracted _____ g Final Volume _____ mL
Extraction/Cleanup Procedure _____

Analyte homolog	Concentration (µg/g)	Analyte homolog	Concentration (µg/g)
1-Cl		6-Cl	
2-Cl		7-Cl	
3-Cl		8-Cl	
4-Cl		9-Cl	
5-Cl		10-Cl	
		Total	

Surrogate compound	Concentration (µg/g)	Surrogate compound	Concentration (µg/g)
^{13}C-Cl_1		^{13}C-Cl_8	
^{13}C-Cl_4		^{13}C-Cl_{10}	

Estimated Method LOQ _____

Highest concentration per resolvable chromatographic peak _____ µg/g

Reported by:	Internal Audit:	EPA Audit:
Name	Name	Name
Signature/Date	Signature/Date	Signature/Date
Organization	Organization	Organization

If a peak is confirmed as being a non-PCB, it may be deleted from the calculation (Section 12). If a peak is confirmed as containing both PCB and non-PCB components, it must be quantitated according to Section 12.3.

14.0 Quality Assurance

Each participating laboratory must develop a quality assurance plan (QAP) according to EPA guidelines.[9] Additional guidance is also available.[10] The quality assurance plan must be submitted to the Agency (regional QA officer) for approval prior to analysis of samples.

The elements of a QAP include:

- Title Page
- Table of Contents
- Project Description
- Project Organization and Responsibility
- QA Objectives for Measurement Data in Terms of Precision, Accuracy, Completeness, Representativeness, and Comparability
- Sampling Procedures
- Sample Custody
- Calibration Procedures and Frequency
- Analytical Procedures
- Data Reduction, Validation and Reporting
- Internal Quality Control Checks
- Performance and System Audits
- Preventive Maintenance
- Specific Routine Procedures Used to Assess Data Precision, Accuracy and Completeness
- Corrective Action
- Quality Assurance Reports to Management

15.0 Quality Control

15.1 Each laboratory that uses this method must operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial and continuing demonstration of laboratory capability by the analysis of check samples. The laboratory must maintain performance records to define the quality of data that are generated.

15.2 Certification and performance checks - Prior to the analysis of samples, the laboratory must define its routine performance. At a minimum, this must include demonstration of acceptable response factor precision with at least three replicate analyses; and analysis of a blind QC check sample (e.g., the response factor calibration solution at unknown concentration submitted by the QA officer). Acceptable criteria for the response factor precision and the accuracy of the QC check sample analysis must be presented in the QA plan.

Ongoing performance checks should consist of periodic repetition of the initial demonstration or more elaborate measures. More elaborate measures may include control charts and analysis of QC check samples consisting of other congeners or with matrix interferences.

15.3 Procedural QC - The various steps of the analytical procedure should have quality control measures. These include but are not limited to:

15.3.1 GC performance - See Section 7.1 for performance criteria.

15.3.2 MS performance - See Section 7.2 for performance criteria.

15.3.3 Qualitative identification - At least 10% of the PCB identifications, as well as any questionable results, should be confirmed by a second mass spectrometrist.

15.3.4 Quantitation - At least 10% of all manual calculations, including peak area calculations, must be checked. After changes in computer quantitation routines, the results should be manually checked.

15.4 Sample QC - Each sample and each sample set must have QC measures applied to it to establish the data quality for each analysis result. The recoveries of the surrogates, general spectral data quality, and consistency of the internal standard area are all measures of the data quality on individual samples. Within a sample set, analysis of replicates and standard addition samples are measures of the precision and accuracy, respectively.

15.4.1 The surrogate recoveries must be within an acceptable range, as defined in the QAP, for each sample. Typically, recoveries below 50% are unacceptable, and indicate that the sample(s) must be reanalyzed. Recoveries much greater than 100% indicate interferences, improper tuning, a problem with response factors, or an error in the concentration of the surrogate compound. The trend of low recoveries can be indicative of the cause of the loss. If the lower homologs are poorly recovered, but the higher homologs are recovered quantitatively, volatility or chemical degradation losses may be suspected. If higher homologs are selectively lost, or if the losses are irregular, a fractionation cut on a chromatographic cleanup would be a likely suspect to account for the loss.

15.4.2 The general spectral data quality is indicative of the overall reliability of the data for a sample. The levels of the background, intensity ratios within chlorine clusters, etc., must all be evaluated. If the data quality is marginal, the analyst may footnote results with an explanation regarding any doubts about the data quality. If the data are unacceptable (see Section 11.0), either the GC/MS determination or the entire analysis must be repeated.

15.4.3 An easy and significant assessment of the data quality is the consistency of the internal standard areas. If the internal standard area is consistent, the injection volume was correct and the system is operating within general tolerances (i.e., the chromatography column is transmitting compounds and the spectrometer is detecting them). If the internal standard area does not meet the criteria specified in the QAP, e.g., ± 20% of other injections, the data must be reviewed. If the injection or the GC/MS performance is suspect, the sample should be reanalyzed, or other corrective action taken.

15.4.4 QC for small sample sets - For small sample sets (1-10 samples), the minimum QC requirements can be a heavy burden. Analysts are encouraged to be efficient and group similar samples to increase the size of a set. A set is defined as a group of samples analyzed together by the same extraction/cleanup technique and determined on the GC/MS system on the same day or successive days under the same conditions.

At least one method blank must be run. The blank must be exposed to the same sources of contamination--solvent, glassware, etc.--as the samples. If conditions change, additional blanks must be generated. An example would be a new lot of solvent, or a change in dishwashing protocol.

At least one sample must be run in replicate. Triplicates are preferable, but duplicates may be acceptable. The acceptable precision among replicates must be specified in the QAP.

At least one sample must be analyzed by the standard addition technique. The analyst may select the most difficult sample, based on prior knowledge of the sample set, or a random sample. Two aliquots of the sample are analyzed, one "as is" and one spiked (surrogate spiking and equilibration techniques are described in Section 9.2) with Solution "FSxxx ng PCB" or "SIMxxx pg PCB." If the analyst has no prior knowledge of the sample, the spiking level should be in the middle of the calibrated range for the mass spectrometer. If the concentrations of PCBs are known to be high or low, the amount added should be adjusted so that the spiking level is 1.5 to 4 times the measured PCB level in the unspiked sample. The samples should be analyzed together and the quantitative results calculated. The recovery of the spiked compounds (calculated by difference) must be 70-130%. If the sample is known to contain specific PCB isomers, these isomers may be substituted for solution FSxxx ng PCB or SIMxxx pg PCB.

15.4.5 QC for intermediate sample sets - With intermediate (approximately 10-100 samples) sample sets, the number of method blanks, replicates, and standard addition samples must comprise at least 10% each.

15.4.6 QC for large sample sets - When a large sample analysis program is being planned, the QA plan may propose specific QC measures. If none are proposed, the guidelines for intermediate sets may be followed. One QC measure which may increase efficiency is the use of control charts. If, for example, the control charts establish that there is no blank problem over the long term, the percent of blanks may be reduced. Any changes in the procedure (e.g., a new lot of solvent) will still, of course, require a blank.

15.5 It is recommended that the participating laboratory adopt additional QC practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates or triplicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

16.0 Method Performance

The method has been evaluated using both intra- and interlaboratory studies.[3,11] Both studies must be considered preliminary; only a limited number of matrices and method options have been investigated. The preliminary interlaboratory study involved only four participants and was conducted before the method was ruggedized, so data from that study may not be representative of the potential method performance. Further intra- and interlaboratory validation is anticipated. Preliminary values for limits of quantitation; intralaboratory recoveries, precision, and accuracy; and interlaboratory recoveries, precision, and accuracy are presented in Table 17. The values in the "best" and "worst" columns represent typical extremes of the measurement, ignoring exceptional cases. For example, some mass spectrometers, when running under optimal conditions, can probably quantitate less than 0.5 ng/μL in the full scan mode for some matrices and PCB congeners. On the other hand, the method LOQ will be much greater than the stated value if a high concentration coeluting interference completely obscures any PCB signal, even at the percent level.

The performance values in Table 17 were derived using either the SIM or LMS options of the method and at concentrations at the lower end of the working range. Working in the middle-to-upper concentration ranges with full scan data collection, the precision, recovery, and accuracy should all improve considerably.

The values in Table 17 represent best estimates of the parameters and will be refined as additional intra- and interlaboratory studies produce more data. Performance better than or worse than any of these parameters cannot, of itself, be construed as grounds for acceptable or unacceptable data quality. Performance criteria should be stipulated in the QAP.

17.0 Documentation and Records

Each laboratory is responsible for maintaining full records of the analysis. A detailed documentation plan should be prepared as part of the QAP. Laboratory notebooks should be used for handwritten records. GC/ MS data must be archived on magnetic tape, disk, or a similar device. Hard copy printouts may be kept in addition if desired. QC records should be maintained separately from sample analysis records.

The documentation must describe completely how the analysis was performed. Any variances from the protocol must be noted and fully described. Where the protocol lists options (e.g., sample cleanup), the option used and specifics (solvent volumes, digestion times, etc.) must be stated.

The remaining samples and extracts should be archived for at least 2 months or until the analysis report is approved, whichever is longer, and then disposed unless other arrangements are made. The magnetic tapes of the analysis and hardcopy spectra, quantitation reports, work sheets, etc., must be archived for at least 3 years.

Table 17. Method Performance Parameters

Measurement	Best case	Worst case	Typical value
Instrumental LOQ (ng/µl)			
Full scan	0.5	10	1
Limited mass scan	0.05	0.5	0.1
Selected ion monitoring	0.01	0.2	0.05
Sample concentration factor	1,000→1	1→100	-[a]
Matrix interference level (ng/µl)	< 0.01	> 1,000	-[a]
Sample injection volume (µl)	10	0.1	1
Method LOQ (µg/g)	10^{-5}	500	1
Intralaboratory[b]			
Recovery (%)	90 ± 15[c]	< 50, > 200[d]	70-130
Precision (%)	-	-	± 34%[c]
Accuracy	-	-	-
Interlaboratory[b,e]			
Recovery (%)	-	22-690	-
Precision (%)	-	-	± 60[f]
Accuracy	-	-	± 62[g]

[a]Varies widely from matrix-to-matrix, no "typical value."
[b]Data for preliminary validation at low (< 1 µg/g) levels using selected ion monitoring mass spectrometry.
[c]"Methods of Analysis for By-Product PCBs--Preliminary Validation and Interim Methods," M. D. Erickson, J. S. Stanley, G. Radolovich, K. Turman, K. Bauer, J. Onstot, D. Rose, and M. Wickham, Interim Report No. 4, Washington D.C.: Office of Toxic Substances, EPA-500/5-82-006, October 1982, 243 pp. NTIS No. PB83 127 696.
[d]Values outside the 50-200% range are generally considered unacceptable and the analysis must be repeated.
[e]Preliminary interlaboratory study involving four participants: "Analytical Methods for By-Product and Destruction Derived PCBs--Interlaboratory Validation A," M. D. Erickson, K. M. Bauer, and F. J. Bergman, Draft Interim Report No. 6, Washington, D.C.: Office of Toxic Substances, U.S. Environmental Protection Agency, Draft Interim Report No. 6, Task 51, EPA Contract No. 68-01-5915, August 1983.
[f]Based on a mean of the 10 homolog values from the analysis of two samples by four laboratories.
[g]Based on the deviation of the reported values from the prepared value for 10 homologs x 2 samples x 4 laboratories.

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